



Effectiveness and stability of commercial Pd/C catalysts in the hydrodechlorination of meta-substituted chlorobenzenes

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ABSTRACT

The catalytic properties of commercial Pd/C catalysts containing 3%, 5% and 10% palladium were studied in the hydrodechlorination of five meta-substituted chlorobenzenes. The morphology and structure of the catalysts were investigated by TEM, selected area electron diffraction (SAED), X-ray powder diffraction (XRD) and hydrogen chemisorption. TEM data showed the Pd particles to be distributed uniformly on the carbon surface, their mean size increasing from 2.8 nm to 3.3 nm and 5.3 nm with the Pd loading rising from 3 to 5 and 10%. The mean particle sizes estimated from H₂ chemisorption were greater than those from TEM and it were equal to 4.3, 5.5 and 12.1 nm, respectively. Suppressed H₂ chemisorption was ascribed to carbon contamination of the Pd phase. The hydrogenolysis kinetics of 3-chloroaniline, 1-chloro-3-fluorobenzene, 3-chloroanisole, 1,3-dichlorobenzene and 3-chlorotoluene was investigated in the presence of these catalysts in n-heptane–alkaline aqueous solution at 60 °C and atmospheric pressure of hydrogen. The main reaction products were dechlorinated ones. With all catalysts the initial rates of hydrogenolysis increased in the following sequence: 3-chlorotoluene, 1,3-dichlorobenzene, 3-chloroanisole, 1-chloro-3-fluorobenzene and 3-chloroaniline, and for the most active 10% Pd/C catalyst, corresponding TOFs values were equal to 1.04, 1.12, 1.23, 1.32 and 1.61 (s^{−1}), respectively. Additionally, the stability and effectiveness of the Pd/C catalysts were tested in the presence of aq NaOH or without base, using 3-chlorotoluene as the model compound. Under basic conditions, the 3% Pd/C catalyst was found to be the most stable, but without base the 10% Pd/C catalyst retained its activity for longer than the 3% and 5% Pd/C catalysts. The formation of HCl, as well as leaching of Pd and formation of biphenyls—by-products of the hydrogenolysis reaction, were probably the main reasons for catalyst deactivation.

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1. Introduction

The hydrogenolysis of organohalogen compounds in the presence of heterogeneous noble metal catalysts plays an important role both as a useful tool in organic synthesis [1–6] and as a potential method for the treatment of organohalogen wastes [7–9]. Recent decades have witnessed intensive research in the field of hydrogenolysis, especially in dechlorination and defluorination [10]. Dechlorination has been studied in the gaseous [11–18] and liquid phases [19–36]. Although many metals, e.g., Ni, Pt, Rh, Ru and Pd [10,12–14,35,36], have the ability to catalyse the hydrogen-for-chloride substitution in chloroaliphatics [13,17,18] and chloroaromatics [12,14–16,19–36], palladium (Pd) displays special features. It is the most efficient metal in dechlorination and, unlike nickel and platinum, is least effective in the hydrogenation of aromatic rings at

low temperatures [6]. Pd supported on alumina and on various carbons is preferred [9], but other supports such as TiO₂, MgO and ZrO₂ have been also applied [9]. Pd/C catalysts are very widely used in research laboratories and in the chemical industry [6]. These catalysts have a high surface area and are chemically extremely stable in aggressive environments. The unique efficiency of carbon-supported Pd in the hydrodechlorination of chloroaromatic compounds has been demonstrated in both the gaseous [13,15] and the liquid phase [23–27]. Liquid-phase hydrodechlorination has been studied in one liquid medium with [23–26] and without a base [19,27], as well as in two liquids [28–33]. Interesting results were obtained using alkaline aqueous-iso-octane [28–30] and alkaline aqueous-n-heptane systems [32,33]. In a previous paper we discussed the influence of various experimental conditions such as temperature, base concentration and the speed of stirring of the reaction mixture on the hydrodechlorination of chlorobenzene over a Pd/C catalyst [32]. Recently, we also put forward a detailed kinetic model for the hydrogenolysis of o-chlorotoluene in the presence of Pd/C catalysts [33].

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Generally, it was found that the hydrodechlorination of chloroaromatic compounds over supported palladium depends on the catalyst synthesis, nature of the support and Pd loading [9,22], solvent [25], base addition [20,21,32,33] and the Pd particle size [22,34]. However, a role of metal particle size on the activity of the Pd catalysts in the hydrogenolysis reaction is not clear although it has been studied in gaseous [12,13] and liquid phases [22,34]. Some authors reported increase of the catalyst activity with the decrease of Pd particle size [12,34], while others opposite with the increase of Pd particle size [22]. Additionally, the hydrodechlorination has been considered also as a structure insensitive reaction on Pd catalysts [37].

In this work commercial Pd/C catalysts with a Pd loading of 3%, 5% and 10% were tested for the liquid-phase hydrodechlorination of the following meta-substituted chlorobenzenes: 3-chlorotoluene, 3-chloroaniline, 3-chloroanisole, 1,3-dichlorobenzene and 1-fluoro-3-chlorobenzene. Little information regarding the hydrodechlorination of these compounds is available in the literature [28,38] in comparison to para-substituted analogs [19,27,29,30]. The aim of the present study is to clarify how electronic, inductive and mesomeric effects, influences hydrodechlorination reaction. The effect of metal loadings, catalyst structure and reaction conditions on the effectiveness of hydrodechlorination were investigated in detail. The stability of these catalysts in a hydrogenolytic environment was also examined. Prior to the activity tests, all the Pd/C catalysts were characterised by high-resolution electron microscopy (HRTEM), selected area electron diffraction (SAED), X-ray powder diffraction (XRD) and hydrogen chemisorption in order to correlate their performance with their physiochemical properties.

2. Experimental

2.1. Materials

The catalysts—3% Pd/C, 5% Pd/C and 10% Pd/C, as well as the meta-substituted chlorobenzenes: 3-chlorotoluene (98% purity), 1,3-dichlorobenzene (99% purity), 1-fluoro-3-chlorobenzene (98% purity), 3-chloroanisole (98% purity), 3-chloroaniline (98% purity) and internal standard n-dodecane (>99.9% purity) were purchased from Sigma-Aldrich. The n-heptane (99.5% purity) solvent was supplied by Lab-Scan, sodium hydroxide (p.a. purity) by POCH-Gliwice, and the nitrogen and hydrogen (>99.5% purity) by Linde.

2.2. Catalyst characterisation

The characteristics of the catalysts were as follows: 3% Pd/C – particle size $\sim 10\ \mu\text{m}$, BET surface area $780\ \text{m}^2\ \text{g}^{-1}$; 5% Pd/C – particle size $\sim 45\ \mu\text{m}$, BET surface area $870\ \text{m}^2\ \text{g}^{-1}$; 10% Pd/C – particle size 90% $< 60\ \mu\text{m}$, 10% $< 5\ \mu\text{m}$ BET surface area $880\ \text{m}^2\ \text{g}^{-1}$. TEM images and SEAD patterns were obtained with a Philips CM20 Super Twin microscope, which at 200 kV provides 0.25 nm resolution. Analysis of TEM images was made with ImageJ program [39]. The elemental composition of the catalyst samples was checked with a Philips 515 scanning electron microscope ($E = 30\ \text{kV}$) equipped with an EDS analyser. XRD patterns were obtained using a DRON-3 diffractometer equipped with a Ni-filtered $\text{CuK}\alpha$ radiation source. Prior to characterisation Pd/C catalysts were pre-treated in H_2 at $400\ ^\circ\text{C}$ (heating rate $5\ ^\circ\text{C}/\text{min}$) for 2 h. XRD patterns were also obtained from the Pd/C catalysts without pre-reduction treatment (as received from Sigma-Aldrich).

The dispersion of palladium was determined by the H_2 chemisorption method at room temperature using the conventional volumetric glass apparatus (base pressure of 10^{-6} Torr). Prior to measurements, the Pd/C catalyst ($\sim 0.8\ \text{g}$) was degassed for

30 min at room temperature, then reduced in hydrogen (250 Torr) at $400\ ^\circ\text{C}$ for 2 h and degassed at the same temperature for 2 h. After cooling under vacuum to the adsorption temperature, the total H_2 uptake (adsorption at the Pd surface and absorption in the bulk) was measured. Next, after degassing the catalyst sample at 10^{-6} Torr for 30 min at room temperature, a second isotherm representing mainly hydrogen absorbed in the Pd bulk was measured in the same way.

2.3. General procedure of hydrodechlorination

Hydrodechlorination was performed at $60\ ^\circ\text{C}$ and atmospheric pressure of hydrogen. The catalytic reactions were carried out in a $50\ \text{cm}^3$ two-walled, three-necked, round-bottomed reactor connected to a gas burette supplying hydrogen or nitrogen. The procedures were similar to those described previously [32,33]. The catalysts were used as received since preliminary experiments with the catalysts reduced at $400\ ^\circ\text{C}$ gave similar results. In a typical catalytic experiment, the dry reactor was initially purged with nitrogen flow for a few minutes. The catalyst (30–100 mg) was pre-conditioned prior to the catalytic test by being soaked and stirred for 30 min at 300 rpm in $10\ \text{cm}^3$ of a solution containing 0.25 M of a given meta-substituted chlorobenzene and 0.025 M n-dodecane (internal standard) in n-heptane. During soaking procedure, the burette was filled with nitrogen to ensure the apparatus was leak proof. The stirrer was then stopped and $15\ \text{cm}^3$ 2% aq NaOH was added to the reactor. Next, the burette and the reactor were flushed with hydrogen and finally the burette was filled with hydrogen at atmospheric pressure. The instant the stirrer was turned on again was taken to be the starting point of the catalytic process. The suspension was stirred with an egg-shaped $9.5\ \text{mm} \times 19.1\ \text{mm}$ magnetic stirring bar (Aldrich). The stirring speed was maintained at 2000 rpm with an IKA RH digital magnetic stirrer.

2.4. Analyses

The reaction rate was usually controlled by measuring the H_2 consumption, but occasionally by measuring the quantities of meta-chlorosubstituted and dechlorinated compounds in the n-heptane layer. Since both techniques were found to yield similar results, the n-heptane layer was analysed only at the end of the reaction to ensure whether the hydrodechlorination process had proceeded to completion and to track the final stage of the process. The substrates, dechlorination products and by-products (mainly biphenyls) were analysed by gas liquid chromatography GLC using apparatus as in [32,33]. The Mohre method was used to analyse the chloride ions in the aqueous layers, separated following the completion of the dechlorination process. The extent of hydrodechlorination resulting from assays of these ions agreed within 99% of that estimated from measurements of H_2 consumption and within 92% of that determined from GLC-measured dechlorinated compound contents. An accuracy of the chromatographic assays was better than $\pm 8\%$, that of the chloride ion assays was better than $\pm 0.2\%$. The palladium content in the aqueous layers was analysed by the dithizone method [40] and atomic absorption spectroscopy (AAS).

3. Results and discussion

3.1. Structural characterisation of the catalysts by XRD and TEM

X-ray diffraction profiles of the Pd/C catalysts reduced at $400\ ^\circ\text{C}$ are shown in Fig. 1. The XRD spectra contain peaks corresponding to the (1 1 1) and (2 0 0) planes of the fcc lattice of palladium. The Pd crystallite sizes calculated from the line broadening of Pd (1 1 1) peak are about 7, 9 and 15 nm for the 3%, 5% and 10% Pd/C catalysts,

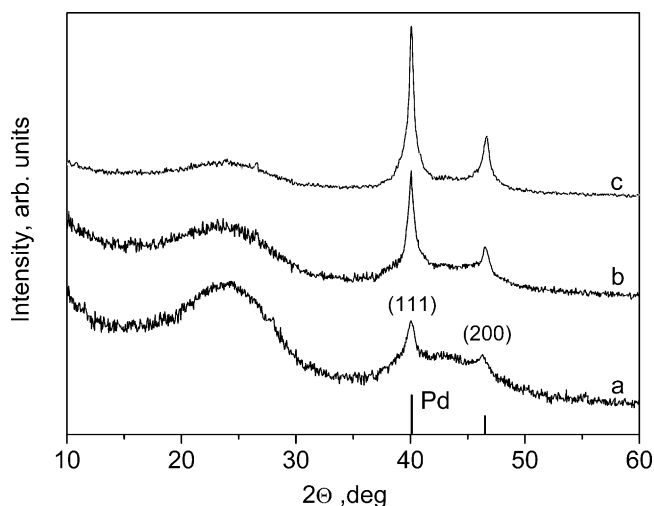


Fig. 1. XRD patterns of 3% Pd/C (a), 5% Pd/C (b) and 10% Pd/C (c) catalysts reduced at 400 °C.

respectively. The XRD profiles include also a very broad peak at $\sim 26^\circ$ characteristic of structured (graphitic) carbon [41]. The XRD patterns obtained from the catalysts without pre-reduction treatment (not shown) contain reflections of metallic Pd and also a very weak reflection at $2\theta = 34^\circ$ corresponding to the PdO phase. The average crystallite size of metallic Pd in these samples was close to that after reduction treatment.

Fig. 2 shows representative TEM micrographs, SAED patterns (insets) and the corresponding Pd particle size distributions of the reduced Pd/C catalysts with the 3% Pd (a), 5% Pd (b), and 10% Pd (c). Analysis of SAED patterns revealed the presence of metallic Pd, which is seen in the TEM images as small, circular but also larger, irregular dark particles. The small Pd particles were nearly uniformly distributed over the carbon support, but in all samples, Pd particles exhibited a broad size distribution (1–25 nm), clearly visible even in the low-loaded catalyst (Fig. 2a). Also, much larger Pd particles up to 35 nm were observed on occasion, in the 5% and 10% Pd/C catalysts. The mean sizes of Pd particles are 2.8 nm, 3.3 nm and 5.3 nm for the 3%, 5% and 10% Pd/C catalysts, respectively. The calculated standard deviation of the mean was 0.8 nm for the 3% Pd/C catalyst and 0.5 nm for the 5% and 10% Pd/C catalysts, respectively.

3.2. Adsorption of hydrogen

It is known that determination of Pd dispersion in supported Pd catalysts, based on H_2 uptake, is complicated by the formation of the bulk Pd hydride in the temperature and pressure range normally used for volumetric chemisorption measurements. In such experiments, the total removal of hydrogen from the supported Pd catalysts is achieved during degassing at temperatures as high as 300–400 °C [42] hence we used reduction/

degassing temperature of 400 °C. As example, Fig. 3 presents the total and reversible isotherms of hydrogen adsorption obtained for the 5% Pd/C catalyst. The both hydrogen isotherms show a linear dependence with pressure in the 100–220 Torr range. Extrapolation of adsorption isotherms to zero pressure was used to determine the amount of irreversibly adsorbed hydrogen. The adsorption results for all Pd/C catalysts are presented in Table 1. Palladium dispersion (H/Pd) was determined from irreversible H_2 uptake, using the chemisorption stoichiometry of $H_{irr}:Pd_s = 1$, where Pd_s is a surface Pd atom [42–44]. As can be seen, Pd dispersion decreased from 0.26 to 0.09 with palladium loading in the Pd/C catalysts. The calculated bulk hydride ratios are also shown in Table 1. The bulk hydride ratio was defined as H_{ab}/Pd_{bulk} , where H_{ab} represents the uptake based on reversible H_2 uptakes at 140 Torr and $Pd_{bulk} = Pd_{total} - Pd_s$ [42,45]. The H_{ab}/Pd_{bulk} ratio reaches a value of 0.59–0.58 for 3% and 10% Pd/C catalysts as compared to 0.71 for the 5% Pd/C catalyst. The maximum hydride value found for bulk Pd is ~ 0.66 at room temperature [46]. Thus, reasonable hydride ratios for all Pd/C samples were obtained.

Table 1 presents also the average Pd particle sizes in the Pd/C catalysts obtained using the different methods. The mean particle size estimated from H_2 chemisorption deviates significantly from that obtained by TEM and XRD. Similar discrepancies can be found in the literature [42,47,48]. The discrepancy between TEM and XRD may be attributed to the broad particle size distribution, especially the large population of small particles, 1–4 nm, overlooked by XRD. The lack of correspondence between chemisorption and TEM data may indicate substantial suppression of hydrogen chemisorption due to the blockage of the Pd surface by carbon atoms. Also, Krishnakutty and Vannice reported suppression of hydrogen chemisorption on carbon-supported Pd [42] and concluded that during chemisorption measurements the Pd crystallites become contaminated by C atoms. Similarly, Amorim and Keane [48] found for Pd/C catalysts a significant difference (by up to a factor of 3) in the average Pd particle sizes obtained by H_2 chemisorption and TEM, attributing this to the widely accepted but unwarranted assumption of an exclusive H_2/Pd adsorption stoichiometry = 1/2. Our commercial Pd/C catalyst samples were chemically analysed using EDS, which revealed the presence of a small amount of alkali metals (Na ions) and sulphur. Contamination of the Pd phase by these impurities can also decrease the coverage of adsorbed hydrogen [42].

3.3. Hydrodechlorination of meta-substituted chlorobenzenes

In order to compare the effectiveness of the 3%, 5% and 10% Pd/C catalysts in the hydrogenolysis of meta-substituted chlorobenzenes, two sets of experiments were performed. In the first one an equal mass (100 mg) of each catalyst was used (Exp. Set 1), while in the second set an equal Pd mass (30 mg) was applied (Exp. Set 2). An n-heptane solution of the chloroaromatic compound and 2% aq NaOH was used as the reaction medium. The catalyst was suspended mainly in the organic layer. Five meta-substituted chlorobenzenes (see Table 2) were hydrogenolysed and the

Table 1

Hydrogen uptakes, palladium dispersions, bulk hydride ratios and the average Pd particle sizes obtained by H_2 chemisorption, TEM and XRD methods for the Pd/C catalysts.

Catalyst	Irreversible H_2 uptake ($\mu\text{mol/g cat.}$)	Dispersion (H/Pd)	Reversible H_2 uptake ^a ($\mu\text{mol/g cat.}$)	Bulk hydride ratio (H_{ab}/Pd_{bulk})	Average size of Pd particles (nm)		
					$d(\text{chem})^b$	$d(\text{TEM})^c$	$d(\text{XRD})$
3% Pd/C	36.60	0.26	62.0	0.59	4.3	2.8	7.0
5% Pd/C	48.0	0.20	134.0	0.71	5.5	3.3	9.0
10% Pd/C	43.0	0.09	247.0	0.58	12.1	5.3	15.0

^a At pressure of 140 Torr.

^b Calculated from H_2 chemisorption using relation $d_{av} [\text{nm}] = 1.12/(H/Pd)$ [46].

^c The average size of the Pd particles was calculated by the equation: $d_{av} = \sum n_i d_i / \sum n_i$, where n_i is the number of particles of diameter d_i and $\sum n_i > 600$.

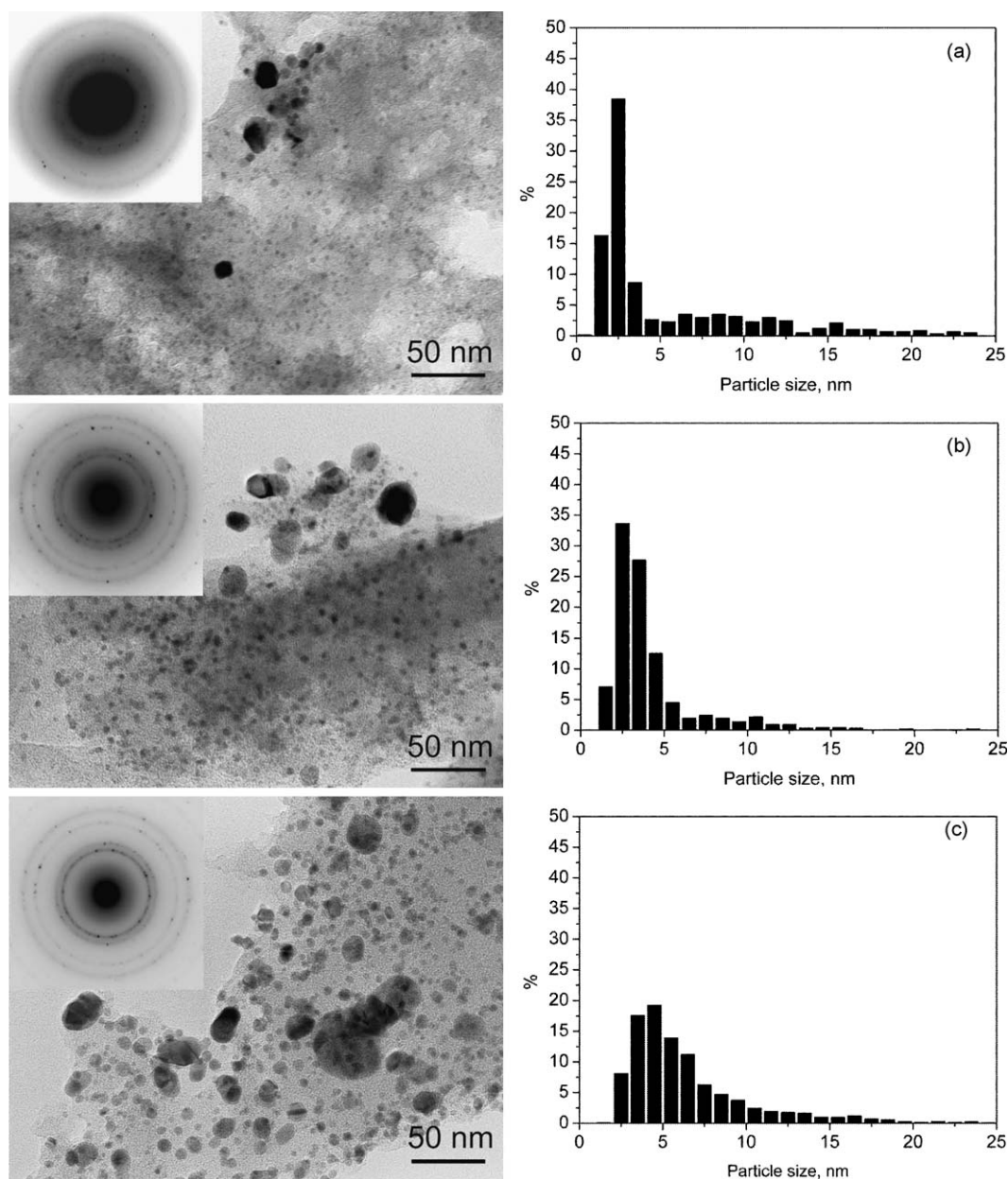


Fig. 2. Representative TEM micrographs, SAED (as inset) and the corresponding Pd particle size distributions of reduced Pd/C catalysts with 3% Pd (a), 5% Pd (b), and 10% Pd (c).

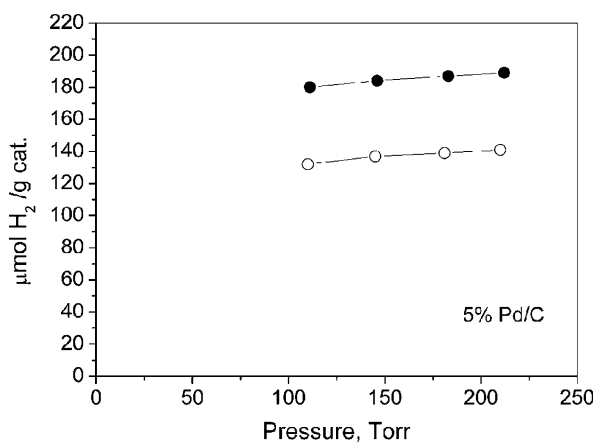


Fig. 3. Isotherms for H_2 adsorption (●, ○) on the 5% Pd/C catalyst. Close and open symbols represent the respective total and reversible H_2 uptakes at room temperature.

principal reaction product formed from the mono-chlorosubstituted compound is a dechlorinated one. However, 1,3-dichlorobenzene undergoes dechlorination to yield chlorobenzene and benzene in the first step. For example, after 50% moles of stoichiometric H_2 uptake, the n-heptane layer contains 46% 1,3-

Table 2

Substrates and products of hydrogenolysis in aq NaOH + n-heptane in the presence of 3% Pd/C, 5% Pd/C and 10% Pd/C catalyst at atmospheric pressure of hydrogen.

	Substrate	Hydrogenolysis products	Final product of hydrogenolysis
1	3-Chloroaniline	Aniline	Aniline
2	3-Chloroanisole	Anisole	Anisole
3	3-Chlorotoluene	Toluene	Toluene
4	1,3-Dichlorobenzene	Chlorobenzene, benzene ^a	Benzene
5	1-Chloro-3-fluorobenzene	Fluorobenzene	Benzene

^a After 50% stoichiometric uptake of hydrogen the n-heptane layer contained 46% 1,3-dichlorobenzene, 9% chlorobenzene and 45% benzene.

Table 3

Kinetic characteristics of the hydrogenolysis of some m-substituted chlorobenzenes over 3%, 5% and 10% Pd/C catalyst in 2% aq NaOH + n-heptane. Atmospheric pressure of hydrogen, temperature 60 °C, stirring speed 2000 rpm, magnetic stirrer 19 mm × 9 mm, equal masses of catalysts (Exp. Set 1).

Compound	100 mg 3% Pd/C ^a		100 mg 5% Pd/C ^a		100 mg 10% Pd/C ^a	
	r_{OB} [M s ⁻¹] ^b	Initial TOF [s ⁻¹] ^b	r_{OB} [M s ⁻¹] ^b	Initial TOF [s ⁻¹] ^b	r_{OB} [M s ⁻¹] ^b	Initial TOF [s ⁻¹] ^b
3-Chloroaniline	1.07×10^{-3}	1.46	1.28×10^{-3}	1.36	1.37×10^{-3}	1.61
1-Chloro-3-fluorobenzene	1.03×10^{-3c}	1.40 ^c	1.06×10^{-3c}	1.13 ^c	1.12×10^{-3c}	1.32 ^c
	7.54×10^{-5d}	0.10 ^d	9.41×10^{-5d}	0.10 ^d	1.04×10^{-4d}	0.12 ^d
3-Chloroanisole	9.96×10^{-4}	1.36	1.01×10^{-3}	1.07	1.04×10^{-3}	1.23
1,3-Dichlorobenzene	8.79×10^{-4}	1.20	9.14×10^{-4}	0.97	9.51×10^{-4}	1.12
3-Chlorotoluene	7.96×10^{-4}	1.09	8.53×10^{-4}	0.91	8.82×10^{-4}	1.04

^a Catalyst quantity and loading.

^b r_{OB} : initial rate, initial TOF for the reaction with base.

^c Values for C–Cl hydrogenolysis.

^d Values for C–F hydrogenolysis.

dichlorobenzene, 9% chlorobenzene and 45% benzene. Hydrogenolysis of 1-chloro-3-fluorobenzene proceeds also in two steps. In the first step, fluorobenzene was formed which then undergoes defluorination to yield benzene as the final product. After 50% stoichiometric uptake of hydrogen in the n-heptane layer no benzene and chlorobenzene was found. Consecutive dechlorination and debromination was also reported by Aramendia et al. [19] for 1-bromo-4-chlorobenzene.

The kinetic data from Exp. Set 1 and Set 2 are presented in Tables 3 and 4, respectively. The initial kinetic rates (r_{OB}) were obtained from the linear fit to the time-dependence of dechlorinated compound concentration (derived from hydrogen consumption) at the starting period, as shown in Fig. 4. This procedure was verified in separate experiments [32,33]. The kinetics obtained is zero order for all compounds up to 50% of hydrogenolysis. It was found that the chemical reaction is the slowest step of the overall process [32,33] so it is taken as a rate determining step. Turnover frequencies (TOFs) were calculated using the initial rates and H₂ chemisorption results (Table 1). The kinetic characteristics presented in Table 3 show that for each meta-substituted chlorobenzene tested, the initial rate of reaction increases slightly with the increase Pd loading in the Pd/C catalyst. Moreover, for the hydrogenolysis of 1-chloro-3-fluorobenzene, defluorination process is much slower than the dechlorination process. For all catalysts, the initial hydrogenolysis rates increase in the following sequence: 3-chlorotoluene, 1,3-dichlorobenzene, 3-chloroanisole, 1-chloro-3-fluorobenzene and 3-chloroaniline. This increase is not however significant. A similar trend was observed for initial TOFs: these values calculated for the hydrogenolysis of 3-chloroaniline on Pd/C catalysts were about 34–55% higher than the ones obtained for the hydrogenolysis of 3-chlorotoluene. It is surprising that kinetic rates of meta-substituted chlorobenzenes, with substituents having fairly different Hammett coefficients as F

and CH₃, show such small differences in reactivity. Similarly, small differences in hydrodechlorination rates for ortho-, meta- and para-substituted chlorobenzenes are reported in literature [19,29,33]. Thus, we think that the Hammett relation fails in explaining of our catalytic data. We suppose rather that rates of hydrogenolysis may be correlated with the change in electronegativity of the heteroatom bound to the chlorobenzene ring. The relevant Pauling electronegativities are: 3.98 for fluorine, 3.44 for oxygen, 3.16 for chlorine, 3.04 for nitrogen, and 2.55 for carbon. The dependence of initial kinetic rate of hydrogenolysis of meta-substituted chlorobenzenes and Pauling electronegativities in the presence of 10% Pd/C is presented in Fig. 5. It shows good linear correlation with $R = 0.98$. However, the detailed mechanism of the hydrogenolysis in examined system is rather complex. Some researchers report that the hydrodechlorination of chlorobenzenes starts with an electrophilic attack of activated hydrogen onto the aromatic ring [19,49] while others think it is nucleophilic [25] or radical reaction [25]. It is quite possible that the reaction may proceed by radical mechanism. Apart from relatively low dependence of reaction rate on electronic properties of substituent, the presence of biphenyl in the reaction mixture also proves a radical mechanism of dechlorination of examined compounds.

The exception is 3-chloroaniline (see Table 3), which shows the highest initial rate of reaction, in spite of the rather low electronegativity of the nitrogen atom. In our opinion, this behaviour can be explained mainly by the basic properties of aniline. It is well known that hydrogen chloride is produced during hydrogenolysis of organochlorine compounds in the liquid phase. The following reactions take place for linear (R) and aromatic

Table 4

Kinetic characteristics of the hydrogenolysis of some m-substituted chlorobenzenes over 3%, 5% and 10% Pd/C catalysts in 2% aq NaOH + n-heptane. Atmospheric pressure of hydrogen, temperature 60 °C, stirring speed 2000 rpm, magnetic stirrer 19 mm × 9 mm, equal amounts of palladium (Exp. Set 2).

Compound	Initial TOF [s ⁻¹] ^a		
	100 mg 3% Pd/C ^b	60 mg 5% Pd/C ^b	30 mg 10% Pd/C ^b
3-Chloroaniline	1.46	1.54	1.83
1-Chloro-3-fluorobenzene	1.40 ^c ; 0.10 ^d	1.50 ^c ; 0.09 ^d	1.71 ^c ; 0.13 ^d
3-Chloroanisole	1.36	1.45	1.62
1,3-Dichlorobenzene	1.20	1.30	1.53
3-Chlorotoluene	1.09	1.25	1.39

^a Initial TOF for the reaction with base.

^b Catalyst quantity and loading.

^c Values for C–Cl hydrogenolysis.

^d Values for C–F hydrogenolysis.

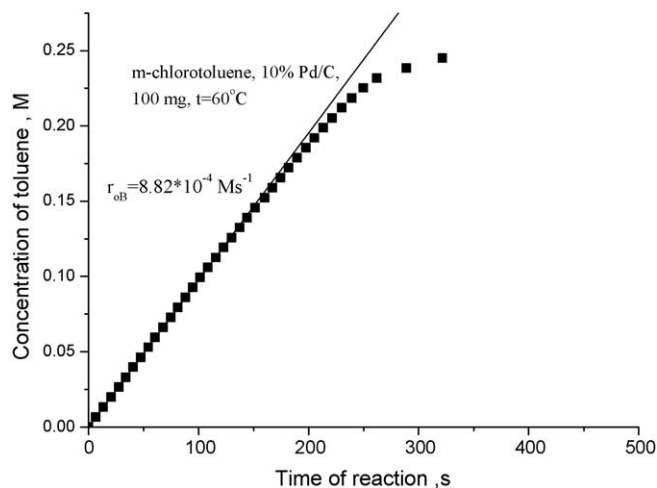


Fig. 4. Time plot of toluene formation in Exp. Set 1 in the presence of 100 mg 10% Pd/C. Atmospheric pressure of hydrogen, temperature 60 °C, stirring speed 2000 rpm.

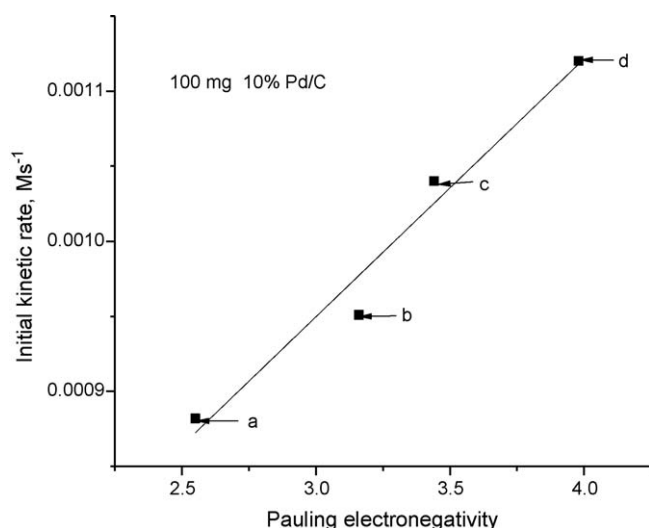


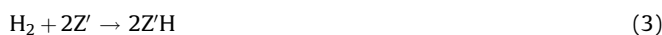
Fig. 5. Initial kinetic rates of hydrogenolysis of meta-substituted chlorobenzenes versus Pauling electronegativities of the heteroatom bound to the chlorobenzene ring in the presence of 100 mg 10% Pd/C. (a) 3-Chlorotoluene, (b) 1,3-dichlorobenzene, (c) 3-chloroanisole, (d) 1-chloro-3-fluorobenzene.

hydrocarbons (Ar):

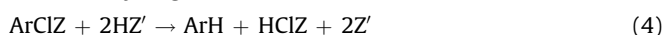


According to the Langmuir–Hinshelwood mechanism [33], the following sequence of processes can be ascribed to this overall reaction (1) or (2) [14]:

- dissociative adsorption of hydrogen at active metal sites,



- reaction of the adsorbed chloroaromatic compound with adsorbed hydrogen,



- removal of hydrogen chloride from the active site



Finally, hydrogenolysis in liquid systems requires the fast and efficient removal of hydrogen chloride from the catalyst surface (reaction (5)) [1,2,9,23,35]. According to literature reports [1,2,31,32], a base added to the reaction mixture increases the rate and yield of hydrogenolysis over a Pd catalyst in liquid systems. The impact of NaOH concentration in two liquid system in hydrodechlorination of chlorobenzene was thoroughly investigated in our previous work [32]. It was found that in the absence of base the rate of hydrogenolysis was an order of magnitude slower than with a base. In the case of 3-chloroaniline it is quite possible that the main hydrogenolysis product (aniline) binds hydrogen chloride and hence additionally increases the rate of reaction, more so than with the aqueous solution alone. It should be stated that a similar effect for the hydrogenolysis of chloropyridines due to the effect of pyridine neutralising the hydrogen chloride released has been reported in the literature [49,50].

Table 4 lists the hydrogenolysis kinetic characteristics of meta-substituted chlorobenzenes in the presence of the same amount of supported palladium (30 mg) (Exp. Set 2). For each hydrodechlorinated compound, initial TOFs increase with Pd loading and are the highest for the 10% Pd/C catalyst despite of this catalyst have a rather low metal dispersion ($\text{H}/\text{Pd} = 0.09$; Table 1). These

data may suggest that the hydrogenolysis is to some extent a structure-sensitive reaction, with the catalyst having the larger, more active Pd particles. The role played by metal particle size on Pd catalyst activity in hydrogenolysis has been studied in the gaseous [12,13,51,52] and liquid phases [22,34,37]. However, there is no general consensus on the structural sensitivity of the hydrodehalogenation reaction on supported Pd catalysts. Some authors have found that this reaction is not sensitive to the structure of Pd catalysts [37], while others have reported an increase activity with decreasing Pd particle size [12,34]. In accord with our data, Gopinath et al. [13] reported an increase in catalyst activity with increasing Pd particle size. In our case, another possibility is that the poisoning of the active phase by the chlorine ions formed during the reaction is less when the Pd particle size increases. In a study of the liquid-phase hydrodechlorination of chlorobenzene over different Pd catalysts, Aramendia et al. [22] also found resistance to chlorine deactivation when the size of metallic particles increased. Similarly, Kovalchuk and d'Itri [52] explained the inhibition of the dechlorination reaction by the stronger interaction of the Cl ions with the smaller metal particles. Some effect of Pd surface blockage by carbon atoms, especially important in the case of small Pd particles, as evidenced by hydrogen chemisorption and TEM data, on the catalytic activity of the Pd/C catalysts cannot be excluded.

3.4. Stability of Pd/C catalysts in a hydrogenolytic environment

The stability of supported palladium catalysts used in liquid-phase reactions, especially under aggressive conditions, is a very important problem [53,54]. In this study, the stability of the Pd/C catalysts was tested both in the presence of aq NaOH or in absence of base, using 3-chlorotoluene as the model compound (Exp. Set 3). Hydrogenolysis was conducted in two stages. In the first one, 15 cm³ 0.245 M 3-chlorotoluene was hydrogenolysed in the presence of 100 mg 3%, 5% and 10% Pd/C catalysts but without aq NaOH. Then, after 54 min, 15 cm³ 2% aq NaOH was added to the reaction mixture. The results are presented in Fig. 6 and Table 5. As shown on Fig. 6 hydrogenolysis over the 10% Pd/C catalyst starts with a reaction rate $r_{\text{ON}} = 9.42 \times 10^{-5} \text{ M s}^{-1}$, then decreases to $r_{\text{IN}} = 3.18 \times 10^{-5} \text{ M s}^{-1}$ and after the addition of base increases rapidly to $r_{\text{2B}} = 1.14 \times 10^{-3} \text{ M s}^{-1}$. It is evident that the reaction rate of hydrogenolysis without base is an order of magnitude lower than that in the presence of base. Subsequent addition of aqueous solution of NaOH to the reaction mixture quickly increases this

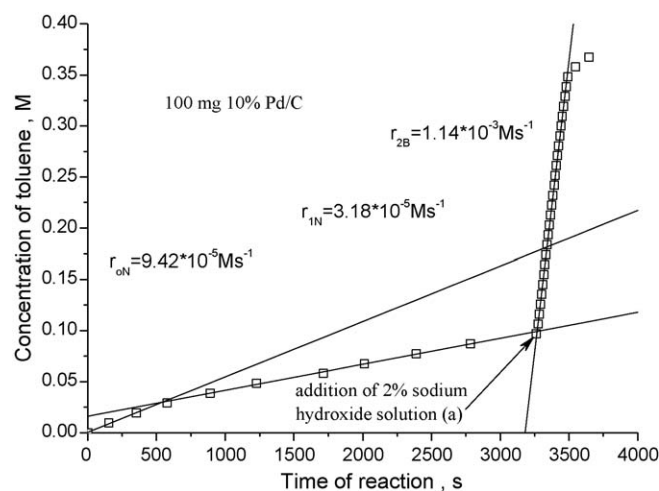


Fig. 6. Time plot of toluene formation in Exp. Set 3 in the presence of 100 mg 10% Pd/C. First stage without aq NaOH. Second stage (a) addition of 15 cm³ 2% aq NaOH. Atmospheric pressure of hydrogen, temperature 60 °C, stirring speed 2000 rpm.

Table 5

Kinetic characteristics of the hydrogenolysis of 3-chlorotoluene over 100 mg 3%, 5%, 10% Pd/C catalyst, atmospheric pressure of hydrogen, temperature 60 °C, stirring speed 2000 rpm, magnetic stirrer 9 mm × 19 mm. First stage without base: 15 cm³ 0.245 M 3-chlorotoluene in heptane. Second stage: addition of 15 cm³ 2% aq NaOH to the reaction mixture^a (Exp. Set 3).

Catalyst	r_{0N} [M s ⁻¹] ^b	r_{1N} [M s ⁻¹] ^c	r_{2B} [M s ⁻¹] ^d
3% Pd/C	2.24×10^{-5}	1.19×10^{-5}	5.92×10^{-4}
5% Pd/C	6.51×10^{-5}	2.82×10^{-5}	9.71×10^{-4}
10% Pd/C	9.42×10^{-5}	3.18×10^{-5}	1.14×10^{-3}

^a See general procedure for hydrogenolysis.

^b r_{0N} : initial rate, for the reaction without base.

^c r_{1N} : rate for the hydrogenolysis without base, post-initial period.

^d r_{2B} : initial rate for reaction after addition of 2% aq NaOH.

characteristic to value observed in a typical procedure with base added at the beging of hydrogenolysis. These observations prove that HCl poisons palladium catalyst and aqueous solution of NaOH greatly improves reaction efficiency. The time plots of hydrogenolysis obtained with 3% and 5% Pd/C catalysts are similar in shape, although there are some differences in the kinetic characteristics (see Table 5). Table 5 indicates that initial rates (r_{0N} , r_{1N} and r_{2B}) increase with Pd loading in the Pd/C catalyst. However, the hydrogenolysis rate of 3-chlorotoluene over the 3% Pd/C catalyst, after addition of 2% aq NaOH, was lower ($r_{2B} = 5.92 \times 10^{-4} \text{ M s}^{-1}$) than the initial rate obtained in the general procedure with the addition of the base solution at the beginning of the reaction ($r_{0B} = 7.96 \times 10^{-3} \text{ M s}^{-1}$; see Table 3). On the other hand, r_{2B} for 5% and 10% Pd/C ($9.71 \times 10^{-4} \text{ M s}^{-1}$, $1.14 \times 10^{-3} \text{ M s}^{-1}$) are a little higher than r_{0B} ($8.53 \times 10^{-4} \text{ M s}^{-1}$, $8.82 \times 10^{-4} \text{ M s}^{-1}$, respectively). This result may indicate that the 3% Pd/C catalyst in the absence of base is less stable than the 5% and 10% Pd/C catalysts. Probably, the large fraction of the small Pd particles in the 3% Pd/C catalyst is poisoned more by hydrochloric acid, a reaction by-product, than by the much larger Pd particles present in the 5% and 10% Pd/C catalysts. Some authors suggest that not only the formation of HCl during the course of reaction, but also coke deposition and metal particle sintering, are the possible reasons for catalyst deactivation [22,55]. Thus, we performed additional structure examination of the used Pd/C catalysts collected after the reaction. All used Pd/C catalysts show similar XRD patterns (not shown) to that of the fresh one (see Fig. 1). Also, TEM studies indicated that after reaction Pd particles were not agglomerated and the mean metal particles sizes were comparable to those before reaction. Therefore, we suppose that under applied reaction conditions sintering of the metal phase not occurs.

In another experiment (Exp. 4), hydrogen consumption during the hydrogenolysis of 3-chlorotoluene over 10% Pd/C, also without any base, was measured. The time plot of hydrogen consumption is shown in Fig. 7. The reaction conditions were as in the first stage of the previous experiments (Exp. 3). The hydrogenolysis starts with a rate of hydrogen uptake equal to $r_{0N}^H = 8.64 \times 10^{-7} \text{ mole s}^{-1}$, then it slows to $r_{1N}^H = 1.60 \times 10^{-7} \text{ mole s}^{-1}$ and continues at that rate until 100% stoichiometric uptake, required for chlorine substitution, is reached. The consumption of hydrogen, however, does not stop and the final rate of hydrogen uptake is $r_{2N}^H = 6.67 \times 10^{-8} \text{ mole s}^{-1}$. This additional hydrogen consumption is connected with the hydrogenation, which leads to the saturation of the toluene ring. This was in fact checked against chromatographic analyses of the reaction mixture: the methylcyclohexane concentration in the n-heptane layer was found to grow continuously. Hydrogenation of the aromatic ring was never observed during the hydrogenolysis of all the compounds studied in the presence of aq NaOH (Table 2). The observation that the aromatic ring is not hydrogenated under more basic conditions is also consistent with findings that the activity for benzene hydrogenation on Pd increased on acid supports [56].

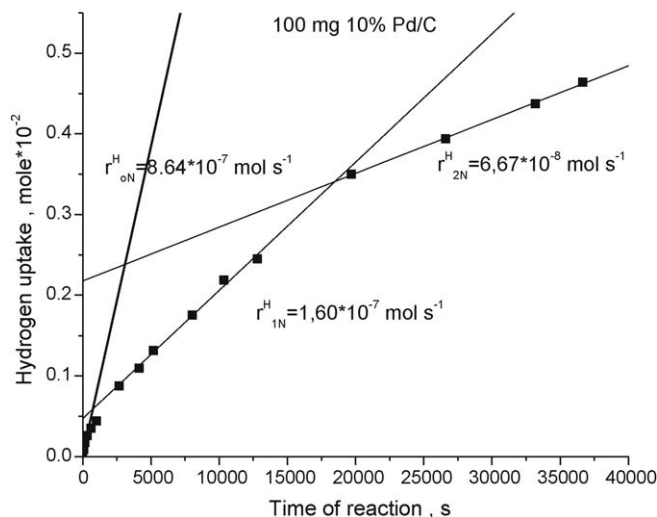


Fig. 7. Time plot of hydrogen uptake in hydrogenolysis of m-chlorotoluene without aq NaOH over 100 mg 10% Pd/C (Exp. 4). Atmospheric pressure of hydrogen, temperature 60 °C, stirring speed 2000 rpm.

The stability of the 3% and 10% Pd/C catalysts was assessed during the multiple hydrogenolysis of 3-chlorotoluene in the presence of the basic solution (Exp. Set 5). 2% and 30% solutions of NaOH were used with the intention of finding out how such a difference in the base concentration influences reaction kinetics and the susceptibility of the Pd phase to leaching. The 3-chlorotoluene was introduced to the reactor system in three successive portions. Figs. 8 and 9 show the respective time plots of toluene production over 10% Pd/C and 30% NaOH and over 3% Pd/C and 2% NaOH. The kinetic characteristics of all the studied systems are presented in Table 6. Clearly, the 10% Pd/C catalyst in the presence of 30% aq NaOH is less stable than in the presence of 2% aq NaOH, and is also less stable than the 3% Pd/C catalyst at both aq NaOH concentrations. In the presence of 30% aq NaOH, the 10% Pd/C catalyst (Fig. 8) displays an initial rate of $r'_{0B} = 8.01 \times 10^{-4} \text{ M s}^{-1}$, on addition of the second portion of 3-chlorotoluene the rate is $r''_{0B} = 3.09 \times 10^{-4} \text{ M s}^{-1}$, but on addition of the third portion it is only $r'''_{0B} = 1.92 \times 10^{-4} \text{ M s}^{-1}$. On the other

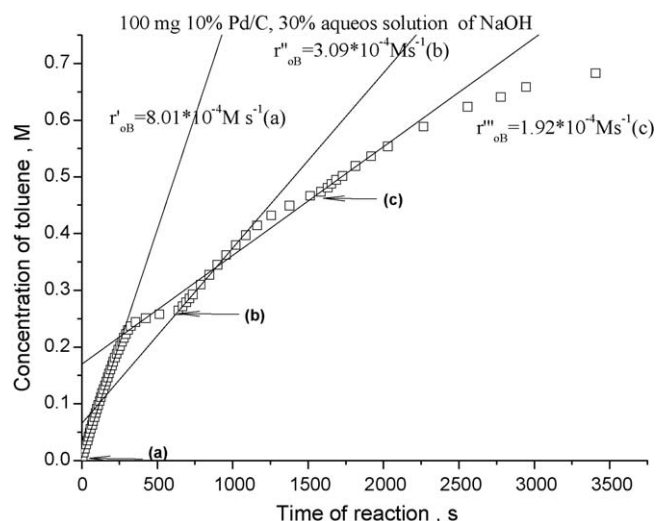


Fig. 8. Time plot of toluene formation in hydrogenolysis with the successive addition of three portions ($2.45 \times 10^{-3} \text{ mole}$) of m-chlorotoluene (Exp. Set 5). 100 mg 10% Pd/C and 30% aq NaOH, atmospheric pressure of hydrogen, temperature 60 °C, stirring speed 2000 rpm. (a) First portion of m-chlorotoluene, (b) second portion of m-chlorotoluene, (c) third portion of m-chlorotoluene.

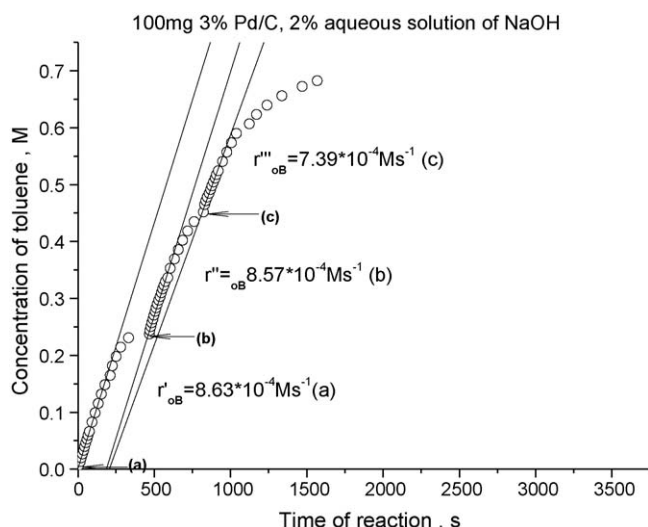


Fig. 9. Time plot of toluene formation in hydrogenolysis with the successive addition of three portions (2.45×10^{-3} mole) of m-chlorotoluene (Exp. Set 5). 100 mg 3% Pd/C and 2% aq NaOH, atmospheric pressure of hydrogen, temperature 60°C stirring speed 2000 rpm. (a) First portion of m-chlorotoluene, (b) second portion of m-chlorotoluene, (c) third portion of m-chlorotoluene.

hand, the 3% Pd/C catalyst in the presence of 2% aq NaOH clearly seems to be the most stable system (Fig. 8 and Table 6). The same catalyst in the presence of 30% aq NaOH is not as stable, although it remains active for a longer time in comparison with the 10% Pd/C catalyst. Thus, in accord with literature data [20], base concentration has a definite impact on the catalyst performance, especially influence on the reactant/catalyst interactions where the surface charge and pH at the interface become crucial.

It is known from literature data that the main reason for the deactivation of Pd catalysts used in liquid-phase hydrodechlorination reactions is leaching of the active metal [53,54]. Deactivation generally depends on the reaction conditions (pH, oxidation potential, chelating properties of molecules etc.) and on the bulk and surface properties of the metal [54]. To determine soluble Pd species, the aqueous layers separated on completion of the dechlorination conducted in experiments of Set 5 were analysed. The amounts of Pd (in wt.%) leached from the 3% and 10% Pd/C catalysts are given in Table 7. This shows that the only significant leaching of palladium occurred with the 10% Pd/C catalyst in the presence of the 2% NaOH solution leached only 0.17 wt.% Pd. Thus, it is possible that such significant leaching of Pd from this catalyst is due to the high concentration of base in the reaction mixture. However, in the case of the 3% Pd/C catalyst at both NaOH concentrations, Pd leaching was insignificant. According to some literature data, however, larger Pd particles are more likely to be leached since larger particles form the Pd- β -hydride more easily

Table 7

Leaching of palladium from 100 mg 3%, 5%, 10% Pd/C catalyst in aq NaOH+n-heptane and the extent of biphenyl by-product formation after hydrogenolysis with the successive addition of three portions of 2.45×10^{-3} mole of 3-chlorotoluene, atmospheric pressure of hydrogen, temperature 60°C , stirring speed 2000 rpm, magnetic stirrer 9 mm \times 19 mm (Exp. Set 5).

Catalyst	Concentration of NaOH	Palladium leached [wt%]	Biphenyl detected [M]
3% Pd/C	2% NaOH	0.17	0.84×10^{-3}
3% Pd/C	30% NaOH	0.27	3.17×10^{-3}
10% Pd/C	2% NaOH	0.03	1.69×10^{-3}
10% Pd/C	30% NaOH	1.01	8.34×10^{-3}

[57]. The substantial leaching of Pd from the 10% Pd/C catalyst in the presence of 30% NaOH also caused greater loss of catalytic activity (Table 6). The leached Pd species were probably inactive under the hydrogenolysis reaction conditions used here.

Another reason for the decay of catalytic activity may be the formation of the reaction by-product and its subsequent deposition on the catalyst surface. Therefore, the n-heptane layer was analysed for biphenyl produced by a condensation reaction, i.e. the by-product of the hydrogenolysis of 3-chlorotoluene (see Table 7). The detected concentration of biphenyl rises with the increase in Pd loading in the catalysts, as well as for a given catalyst with aq NaOH concentration. The amount of organic by-product in the n-heptane layer is probably proportional to the amount of biphenyl formed on the catalyst surface. Thus, the higher concentration of biphenyls in the n-heptane layer may explain the greater deactivation of the Pd/C catalysts (Table 7) due to catalyst surface blockage.

The amounts of Pd leached and the biphenyl concentration on completion of the hydrogenolysis reaction in Exp. Set 3 (kinetic data shown in Table 5) were also analysed. In the aqueous phases, 10, 25 and 50 μg of Pd were leached from the 3%, 5% and 10% Pd/C catalysts, respectively. These data show that the amount of Pd leached is proportional to the metal loading in the Pd/C catalysts. Assuming that there is equal access of the leaching medium to all the Pd particles, one may expect that Pd leaching should be directly proportional to the number of surface metal atoms. However, the chemisorption data presented in Table 1 indicate that the difference in the number of surface Pd atoms in the 3%, 5% and 10% Pd/C catalysts was rather small ($<20\%$). Presumably then, Pd leaching may depend on Pd particle size, i.e. the larger particles in the 10% Pd/C catalyst are more likely to be leached than the small particles in the 3% Pd/C sample (Table 1). Since larger Pd particles formed the Pd- β -hydride phase more easily than small Pd particles, it is probable that Pd was leached in the form of the Pd hydride phase. These results are in full agreement with the literature data [57]. On completion of the hydrogenolysis of 3-chlorotoluene over the 3%, 5% and 10% Pd/C catalysts, the concentrations of biphenyls in the n-heptane layers were 1.2×10^{-4} M, 2.0×10^{-4} M and 4.3×10^{-4} M, respectively. It seems that the quantities of biphenyls synthesised depends on the Pd loading in the catalysts. Similar results have been reported by other researchers [58].

Table 6

Kinetic characteristics of the hydrogenolysis of 3-chlorotoluene over 100 mg 3%, 5%, 10% Pd/C catalyst in aq NaOH+n-heptane, atmospheric pressure of hydrogen, temperature 60°C , stirring speed 2000 rpm, magnetic stirrer 9 mm \times 19 mm. Successive addition of three portions of 2.45×10^{-3} mole of 3-chlorotoluene (Exp. Set 5).

Catalyst	Concentration of NaOH	r'_{ob} [M s^{-1}] ^a	TOF'_{ob} [s^{-1}] ^a	r''_{ob} [M s^{-1}] ^b	TOF''_{ob} [s^{-1}] ^b	r'''_{ob} [M s^{-1}] ^c	TOF'''_{ob} [s^{-1}] ^c
3% Pd/C	2% NaOH	8.63×10^{-4}	1.18	8.57×10^{-4}	1.17	7.39×10^{-4}	1.01
3% Pd/C	30% NaOH	7.14×10^{-4}	0.97	6.81×10^{-4}	0.93	5.36×10^{-4}	0.73
10% Pd/C	2% NaOH	8.88×10^{-4}	1.05	5.99×10^{-4}	0.71	4.47×10^{-4}	0.53
10% Pd/C	30% NaOH	8.01×10^{-4}	0.95	3.09×10^{-4}	0.37	1.92×10^{-4}	0.23

^a r'_{ob} : Initial rate, initial TOF'_{ob} after addition of first portion of 3-chlorotoluene.

^b r''_{ob} : Initial rate, initial TOF''_{ob} after addition of second portion of 3-chlorotoluene.

^c r'''_{ob} : Initial rate, initial TOF'''_{ob} after addition of third portion of 3-chlorotoluene.

To summarise, palladium leaching and biphenyl formation are in some extent, responsible for the observed deactivation of the Pd/C catalysts. However poisoning by hydrochloric acid, a reaction by-product seems to be the main cause of the significant deactivation of the Pd/C catalyst.

4. Conclusions

Carbon-supported palladium is highly efficient in the dechlorination of meta-substituted chlorobenzenes in n-heptane-aq NaOH solution. Fluorobenzene is also hydrogenolysed under these reaction conditions, despite the resistance of fluorine to this reaction. The hydrogenolysis rates for meta-substituted chlorobenzenes increases in the following sequence: 3-chloroaniline, 1-chloro-3-fluorobenzene, 3-chloroanisole, 1,3-dichlorobenzene, 3-chlorotoluene. It appears that the initial rates of hydrodechlorination and TOFs on Pd/C catalysts appear to be in agreement with the change in electronegativity of the heteroatom connected to the chlorobenzene ring. The hydrogenolysis reaction rates over Pd/C catalysts were found to be higher in a basic than without base medium, but a smaller base concentration produces higher rates of reaction in contrast to higher base concentrations. The activity data show that under basic conditions the 3% Pd/C catalyst is the most stable. However, without base addition the 10% Pd/C catalyst retained its activity for longer than the 3% and 5% Pd/C catalysts. It was demonstrated that HCl formation palladium leaching and biphenyl formation are responsible for the observed deactivation of the Pd/C catalysts.

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